Bulk Ferroelectric Metamaterial with Enhanced Piezoelectric and Biomimetic Mechanical Properties from Additive Manufacturing

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ABSTRACT: Three-dimensional (3D) ferroelectric materials are electromechanical building blocks for achieving human–machine interfacing, energy sustainability, and enhanced therapeutics. However, current natural or synthetic materials cannot offer both a high piezoelectric response and desired mechanical toughness at the same time to meet the practicality. Here, a lamellar ferroelectric metamaterial was created with a ceramic-like piezoelectric property and a bone-like fracture toughness through a low-voltage-assisted 3D printing technology. The one-step printed bulk structure, consisting of periodically intercalated soft ferroelectric and hard electrode layers, exhibited a significantly enhanced longitudinal piezoelectric charge coefficient ($d_{33}$) of over 150 pC N$^{-1}$, as well as a superior fracture resistance of $\sim$5.5 MPa$\cdot$m$^{1/2}$, more than three times higher than conventional piezo-ceramics. The excellent printability together with the combination of both high piezoelectric and mechanical behaviors allowed us to create a bone-like structure with tunable anisotropic piezoelectricity and bone-comparable mechanical properties, showing a potential of manufacturing practical, high-performance, and smart biological systems.

KEYWORDS: 3D printing, ferroelectric metamaterial, piezoelectricity, biomimetic, mechanical toughness

INTRODUCTION

Recent technology evolutions bring piezoelectric materials to advanced application directions including human–machine interfacing, self-sustainable energy solutions, and revolutionary therapeutic strategies. In these electromechanically coupled systems, strain is an inevitable component. As such, in addition to pursuing high piezoelectric properties, high mechanical toughness is also essential for achieving desired longevity. Typically, soft- or biopiezoelectric materials can offer desired mechanical behaviors but their piezoelectric responses are rather low. Performance-driven developments still primarily rely on piezo-ceramics to leverage their high-piezoelectric responses, which unfortunately are brittle, rigid, and hard to shape. No current natural or synthetic materials can offer both high piezoelectricity and high toughness simultaneously.

An avenue addressing the challenge relies on advanced three-dimensional (3D) printing, a capable manufacturing technique for creating 3D geometries with desired functionality and unusual mechanical fashions. Several 3D printable piezoelectric materials have been developed, such as photoresins incorporating ferroelectric polymers and ceramics, writing inks consisting of volatile solution and ferroelectric solute, as well as thermoplastic filaments made of ferroelectric composites. However, current piezoelectric materials printing is still in its infancy, as many reported piezoelectric prints are actually 2D or 2.5D with low fidelity, weak electromechanical coupling, and poor mechanical properties. Although the highest reported longitudinal piezoelectric charge coefficient ($d_{33}$) of 3D-printed piezoelectric materials from lead zirconate titanate (PZT) composite achieved a value of 110 pC N$^{-1}$, it required an energy-
intensive (extremely high voltage) and hourly long post-fabrication poling, resulting in excessive fabrication time and limited size and dimensionality, together with toxic lead component. The designated hollow structures potentially compromised mechanical robustness as well. Therefore, concurrent 3D-printed piezoelectric materials could hardly meet practical requirements. Here, we adapted the nacre architecture in the design of a lamellar ferroelectric metamaterial to improve its mechanical toughness, where alternating soft ferroelectric and hard electrode layers are directly printed in bulk with an \textit{in situ} poling function through low-voltage-assisted 3D printing (fused deposition modeling, or FDM). The lead-free high-$T_C$ (Curie temperature) Li-KNN with a piezoelectricity comparable to those of lead-based ceramics\footnote{Lead-based ceramics} was blended with poly(vinylidene fluoride)-co-hexafluoropropylene (PVDF-HFP), a dielectric polymer akin to poly(vinylidene fluoride) (PVDF) yet with improved printability,\footnote{Improved printability} to form the ferroelectric layer. The electrode material consisted of highly conductive carbon black fillers (CB) and a common biocompatible printing polymer, poly(lactic acid) (PLA).\footnote{Poly(lactic acid)} The principle for piezoelectricity enhancement was adapted from commercial piezo-stacks and enabled by the development of processable and printable ferroelectric and conductive composites. Thus, manufacturing such a complex multilayered structure by a programmable, autonomous, and low-voltage-assisted additive manufacturing technique becomes possible. The as-fabricated ferroelectric metamaterial exhibited a ceramic-like piezoelectric coefficient ($d_{33}$) and bone-like mechanical toughness, bringing in promises for developing high-performance piezoelectric.

Figure 1. Low-voltage-assisted 3D printing of bulk lamellar ferroelectric metamaterial. (a) Schematics showing the printing process by repeatedly building soft ferroelectric and hard conductive layers. An electric field was applied between the nozzle and conductive layer during the entire printing period. Left insets are scanning electron microscopy (SEM) images of ferroelectric composite (top) and conductive composite (bottom). Bottom insets are schematics of dipole alignment before and after printing. Right insets are schematics of interfacial interaction between Li-KNN MPs and PLA. (b) Finite element analysis (FEA) simulation of potential distribution between the nozzle and printed ferroelectric structure at an applied voltage of 1.4 kV. (c) Long-wave infrared imaging revealing the temperature distribution surrounding the ferroelectric structure during printing. (d) SEM side-view of the as-printed ferroelectric metamaterial showing the lamellar heterostructure. Inset is a digital photo of the as-printed structure. The scale bar is 5 mm. (e) Energy-dispersive X-ray spectroscopy (EDS) mappings of Nb (top) and F (bottom) elements from the side view.
materials. Li-KNN was the key for achieving strong interfacial binding. Therefore, high-fidelity multilayered 3D ferroelectric metamaterial was printed and poled in one step at a constant low voltage. The as-printed material exhibited a significantly enhanced bulk-scale $d_{33}$ of over 150 pC N$^{-1}$, as well as a superior mechanical toughness of ~5.5 MPa·m$^{1/2}$, more than three times higher than those of conventional piezo-ceramics. The excellent printability together with the combination of both high piezoelectric and mechanical behaviors allowed for the creation of bone-like structure with tunable anisotropic piezoelectric responses and bone-comparable mechanical properties.

RESULTS AND DISCUSSIONS

Low-Voltage-Assisted Printing of Lamellar Ferroelectric Metamaterial. The ferroelectric composite filament was made from a mixture of PVDF-HFP polymer and Li-KNN microparticles (MPs) (Movie S1). Compared to pure PVDF,
PVDF-HFP has a much lower crystallinity, avoiding a buildup of stress due to crystallization, while it still provides other akin physical properties (Figure S1 and Section S1). The as-prepared Li-KNN MPs have cube-shaped morphology with size in the range 2–5 μm (Figure S2). Li-KNN is a lead-free ferroelectric material with a piezoelectric property equivalent to lead zirconate titanate (PZT), as well as a high Curie temperature \( T_C \) over 400 °C, allowing its dipole to be pole and retained at the elevated printing temperature (~260 °C).\(^\text{31}\) Because the PVDF-HFP matrix has a \( T_C \) (around 120 °C) far below the printing temperature, the piezoelectricity of the composite is therefore primarily contributed by the Li-KNN particles. After the surface being modified, the Li-KNN MPs exhibited a good compatibility with the PVDF-HFP matrix (mid-left inset of Figure 1a). In order to interface with the soft ferroelectric layer, poly(lactic acid) (PLA) blended with carbon black (CB) was selected to build the hard electrode layer (lower-left inset of Figure 1a). CB nanoparticles with sizes of ~100 nm were well-dispersed in the PLA matrix forming a conductive network. Therefore, the printed electrode layer exhibited a high conductivity of 6.34 S m\(^{-1}\) (Figure S3). This conductivity is at the same level of conductive composites and polymers that have been broadly used as electrodes for bioelectronics and photovoltaics.

As illustrated in Figure 1a, the ferroelectric and conductive filaments were loaded to two nozzles of a 3D printer, respectively. A nozzle with a size ranging from 0.4 to 0.8 mm is appropriate for successful printing for both materials with high fidelity. The bottom electrode layer was printed on the conductive bed first (step I). The ferroelectric layer was then printed on the top of bottom electrode (step II). During this step, an electric field was applied between the nozzle and bottom electrode. Facilitated by the high nozzle temperature, this electric field quickly aligned the dipoles in the just-extruded materials in situ, giving rise to a large net polarization (bottom inset of Figure 1a). Compared to hours-long post poling, the in situ poling largely shortens the fabrication time, demands lower electric field, and prevents the breakdown (failure) of ferroelectric prints. At the interface, the oxide surface of Li-KNN in the ferroelectric layer is expected to form hydrogen bonds with PLA in the electrode layer and thus achieve strong interfacial adhesion (left inset of Figure 1a). Steps I and II could be repeatedly applied to build an alternatively layered 3D metamaterial with programmable piezoelectricity (Figure 1a). By introducing removable conductive buses during printing, a constant voltage of 1.4 kV could be used to achieve in situ poling independent to the number of layers. Finite element analysis (FEA) simulation confirmed that a applied electric field was only concentrated at the nozzle region and was completely screened from other layers by the intercalated electrodes (Figure 1b). This allowed for independent polarization control in each ferroelectric layer. Thermal imaging further showed that, although the nozzle tip had a high temperature of over 200 °C, the heating effect was also mostly concentrated around the nozzle (Figure 1c). Therefore, the previously printed layers stayed around 40–60 °C, which was desired for maintaining the oriented dipoles.

An as-printed 15-layer ferroelectric metamaterial (seven ferroelectric layers) is shown in the inset of Figure 1d, where the white and black layers were ferroelectric and electrode layers, respectively. A cross-sectional scanning electron microscopy (SEM) image shows that the thicknesses of ferroelectric and electrode layers were ~400 μm (each printing layer of 200 μm) (Figure 1d). The printed ferroelectric layer was slightly thicker than the electrode layer, which was mainly because of the higher material flow rate and lower printing speed applied for ferroelectric layers. Although the electrode layer is thicker than the common electrodes in piezoelectric devices, the specific thickness of the electrode layer here is favorable for retaining polarization during printing and achieving a desired mechanical property. Energy-dispersive X-ray spectroscopy (EDS) mapping of the cross-section further confirmed the well-confined distribution of the ferroelectric component (F and Nb elements, Figure 1e) and the conductive component (C and O elements, Figure S4) in alternating layers.

**Piezoelectric Performance of As-Printed Metamaterial.** The ferroelectricity of as-printed material was first examined by polarization hysteresis measured from a single ferroelectric layer, where the remnant polarization reached as high as 27.7 mC m\(^{-2}\) (Figure 2a). The piezoelectric coefficient, \( d_{33} \), of the single layer was then characterized to investigate the influences from the electric field strength. As shown in Figure 2b, when no electric field was applied during printing, \( d_{33} \) was nearly zero. The value of \( d_{33} \) increased almost linearly following the applied electric field and peaked at ~16.1 pC N\(^{-1}\) as the electric field reached 4 kV/mm. Further raising the electric field led to sample breakdown and thus a significant drop of \( d_{33} \). A higher Li-KNN volume fraction could also improve the piezoelectric response. However, higher particle load increased the filament viscosity, which lowered its printability and mechanical stability (Figure S5). Overall, 16.1 pC N\(^{-1}\) was the highest \( d_{33} \) achieved from a single layer with 35% vol Li-KNN, close to the value of commercial PVDF (Figure S6). To further improve piezoelectricity, functionalization reagents can be introduced to covalently bridge both the Li-KNN particle and PVDF-HFP matrix. Besides, the printing can be processed under a more inert environment (such as nitrogen and sulfur hexafluoride) to support a higher in situ poling electric field.

To further enhance the \( d_{33} \), an interdigital electrode configuration with alternating dipole orientation was adapted (Figure 2c). Both ferroelectric and electrode layers were kept at ~400 μm in thickness on the basis of our printer resolution to maximize the number of layers per unit sample height (Section S2). The electrode layers were connected alternately through two separate buses, equivalent to a parallel connection of all piezoelectric units (left inset of Figure 2c). To realize the opposite piezoelectric polarization in adjacent ferroelectric layers, the poling voltage (+1.4 kV, 3.5 kV mm\(^{-1}\)) and ground connections were switched between the nozzle tip and the electrode layers alternatively (Figure S7, with detailed printing process given in Figure S8). While the total voltage applied for the ferroelectric material printing was 1.4 kV, the electric field was remained consistently at 3.5 kV/mm for each printing layer. FEA simulations confirmed that the poling electric field with the same amplitude but opposite direction was exerted on two adjacent units during printing (Figure S7). Because the ferroelectric layer was much softer compared to the electrode layer (Figure S9), the strain would be largely and uniformly concentrated on the ferroelectric layers (pink colored) when subjected to mechanical stimuli (bottom-left inset of Figure 2c). Therefore, all individual ferroelectric films could contribute equivalently to the overall piezoelectric response.

In this configuration, the piezoelectric charges from each ferroelectric film were accumulatively collected. As confirmed
by capacitance measurement, the capacitance increased steadily from 96.53 to 860.33 pF as the number of ferroelectric layers increased from 1 to 7 (Figure 2d). Accordingly, when subjected to an impulse force of 100 N, the piezoelectric current output increased almost linearly with the ferroelectric layer and reached 18.63 μA at seven layers (Figure 2e, Figure S10, Movies S2 and S3). This relatively linear relationship could be attributed to the uniform high quality of each ferroelectric layer and the invariant Li-KNN ferroelectric phase, where the generated charges could be collected accumulatively with minimal loss. Therefore, $d_{33}$ also exhibited a linear increment with ferroelectric layers (approximately 11 pC N$^{-1}$ increment per layer) and reached as high as 80.6 pC N$^{-1}$ at seven layers (Figure 2f). Both equivalent dielectric constant ($\varepsilon_r$) and piezoelectric voltage constant ($g_{33}$) also revealed layer-dependent behaviors, which are presented in
Table S1. Meanwhile, this structure yielded a relatively stable piezoelectric voltage output between 7 and 10 V independent to the number of ferroelectric layers under the same mechanical stimuli (Figure S11). The high piezoelectric output of the 7-ferro-layer metamaterial allowed it to fully power 10 light emitting diodes (LEDs) simultaneously (Figure 2g and Movie S4). By applying a pulsed 100 N force at a frequency of 1 Hz, it could also charge (through a bridge rectifier) a 1 μF capacitor to over 5 V in as short as 120 s, showing a potential in powering small electronics.

The capability of additively integrating ferroelectric layers offered a promising opportunity to create bulk ferroelectric metamaterials with high performances. To demonstrate this potential, a 2S-ferro-layered metamaterial (100 printing layers with each ferro/electrode layer consisting of 2 printing layers) was printed (Figure S12 and Movie S3). Nozzles (0.8 mm) were used, and the ferroelectric material was printed at a printing speed of 10 mm/s while the conductive material was printed at a higher speed of 20 mm/s. The entire printing process took ~2 h. As shown in Figure 2h, this structure had an overall thickness of ~2.5 cm and exhibited a significantly improved d33 of over 150 pC N⁻¹, outperforming the 3D-printed PZT composite (∼110 pC N⁻¹) that required long time postfabrication corona poling. Under the same consecutive impulse force, a stable short-circuit current output of as high as 30.18 μA was recorded, with a corresponding charge output of ~19.72 nC from the ~1.8 cm² material surface (Figure 2h). The open circuit voltage still remained at a stable level of ~6.6 V. Although surface polarization could also be induced by triboelectricity at the contacting interfaces, the piezoelectricity of printed ferroelectric structure is so strong that it makes the contribution from triboelectric effects negligible (Figure S12c). By surveying the electrical output within a wide range of load resistance, the maximum instantaneous power was identified to be 78.34 mW (435.2 mW m⁻²) at a load of 220 kΩ (Figure 2i). This power was more than 1 order of magnitude higher than other 3D-printed energy harvesters/nanogenerators (such as BaTiO₃−poly-(vinylidene fluoride-co-trifluoroethylene) (P(VDF-TrFE)) piezoelectric nanogenerator (14 mW/m²) and 3D-printed triboelectric nanogenerator (23.94−31.39 mW m⁻²)). Alternatively, the piezoelectric voltage could be improved proportionally to the number of layers by connecting the ferroelectric/electrode layers in series (Figure S13 and Section S3).

Study of Interface and Mechanical Property of Lamellar Prints. In addition to its significantly improved and programmable piezoelectricity, this metamaterial also utilized the heterostructure of nacres that possesses superhigh toughness by the periodical integration of hard aragonite platelets and soft biopolymer (proteins and polysaccharides) layers. In our ferroelectric metamaterial, distinct tensile/compressive mechanical moduli were observed in the ferroelectric (0.34/0.47 GPa) and electrode composites (1.70/1.48 GPa). The ferroelectric layer had moduli over three times lower than the electrode layer, mimicking the mechanical property alteration of the soft and hard layers in nacres. Strong bonding between the hard and soft layers is another critical prerequisite to achieve the desired toughness enhancement. As shown by SEM image and EDS mapping in Figure 3a-i, the heterointerface between the ferroelectric and electrode layers exhibited excellent coherency and integrity. The low crystallinity of both polymer matrices successfully avoided layer detachment caused by strain building-up due to crystallization during cooling down. A zoom-in view of the interface provided a clear visualization of the seamless connection between these two layers (Figure 3a-ii). Many Li-KNN MPs could be found at the interface, penetrating into the electrode layer matrix (Figure 3a-iii). Because hydrogen bonds could be formed between oxides and PLA, particularly after high-temperature melting compounding, the Li-KNN MPs were closely wrapped by PLA polymer, contributing to strong interfacial adhesion.

The interfacial adhesion was then confirmed by the Trouser Peel Test, where an as-printed bilayer (ferroelectric and electrode layers) was pulled apart from an initial cleft (Figure 3b). The digital image showed that, while the ferroelectric layer was gradually peeled off, substantial residues remained on both surfaces of the ferroelectric and electrode layers. SEM and EDS revealed that the residues on electrode layer were mainly Li-KNN MPs with a small amount PVDF attached (Figure 3c and Figure S14). Likewise, residues on the ferroelectric layer were carbon-based electrode components. This test showed that the separation partially occurred in the polymer matrix rather than at the interface, evidencing the strong interfacial adhesion force. When no Li-KNN MPs were presented in the polymer matrix, clean peeling surfaces were obtained (Figure S15), further validating the critical contribution from the oxide component. The adhesion force at the PVDF-HFP/Li-KNN and PLA/CB interface was quantified to be ~21 N, 10 times higher than that of the pure PVDF–PLA/CB interface (~2N) (Figure 3d). The adhesion energy was calculated to be 4.06 J/mm² (Section S4), close to the reported values of 3D-printed homogeneous bilayers (such as ABS), suggesting a potential to achieve excellent mechanical integrity.

The high fracture resistance of our lamellar metamaterial was evaluated by a standard single-edge notched bend (SENB) test. The load−displacement curves showed that the electrode composite had a linear elastic response until the catastrophic failure, revealing a crystal-like high strength and high brittleness (Figure 3e). Our ferroelectric metamaterial displayed a similar elastic response before reaching the similar maximal load yet exhibited a considerably large inelastic deformation afterward. The ferroelectric composite, as the “soft layer” in the metamaterial, exhibited a more elastomer-like behavior with a significantly lower load maximum but an equivalently large strain tolerance. The fracture toughness determined from these curves gave a high value of 5.51 MPa m¹/² for our ferroelectric metamaterial (Figure 3f), which was ~50% larger than both ferroelectric and electrode components (Section S5). This value was also over three times higher than those of common ferroelectric ceramics such as PZT and barium titanate (BTO). SEM imaging revealed an apparent crack deflection in our ferroelectric metamaterial (Figure 3g, top, and Figure S16). This cracking behavior could be attributed to the distinct crack driving forces in the soft and hard layers, as well as the strong interfacial bonding in-between, mimicking the toughening mechanism in nacre (Figure S16). Without the soft ferroelectric layer, the crack demonstrated a straight propagation path through the electrode materials (Figure 3g, bottom), resulting in ceramic-like brittleness.

Demonstration of Piezoelectric 3D Structure. The significantly enhanced piezoelectric and mechanical properties placed our ferroelectric metamaterial at an advantageous position for multifunctional implants with complex 3D
geometries. To demonstrate this potential, the piezoelectric metamaterial was designed and printed in the shape of a bone (Figure 4a). All the selected components in both piezoelectric and conductive composites are biocompatible reported in many previous works.45−47 It also should be noted that PLA can slowly degrade in a liquid environment. When a long-term in-liquid application is targeted, PLA may be replaced by other nonwater-dissolvable biopolymers, such as polyetheretherketone (PEEK) or poly(methyl methacrylate) (PMMA). In this demonstration, the as-printed bone-like structure had the same anatomy of the proximal phalange of an index finger. Unlike most reported bone implants, this structure was able to generate piezoelectric potential in response to biomechanical stimuli, just like real bones do. In addition, it could be engineered to show anisotropic piezoelectricity as most natural bones by switching the printing/stacking direction. As shown in Figure 4b, when the stacking direction was along the longitudinal direction, a gentle tapping mimicking biomechanical stimuli caused a voltage spike in the CAE output (Figure 4a). This demonstrated that the developed metamaterial could sense changes in mechanical stress and generate an electric signal.

Figure 4. 3D-printed piezoelectric artificial bones. (a) Schematics of embedded piezoelectric proximal phalange bone in response to human motions. Inset is a digital image of the as-printed piezoelectric bone. Scale bar is 1 cm. (b) Anisotropic piezoelectric response of the artificial bone printed along the long (top panel) and short (bottom panel) axis when subjected to a small impulse force along the vertical and horizontal directions, respectively. (c) Compressive stress−strain curves of (i) 3D-printed PLA/CB (red), ferroelectric metamaterial (blue), and PVDF-HFP/Li-KNN (black) and (ii) 3D-printed ferroelectric metamaterial at equal ferroelectric and electrode layers with different porosities ranging from 0% to 75%. (d) Range of compressive modulus of artificial bones by tuning the composition and porosity. (e) Ashby diagram of fracture toughness versus $d_{13}$ ($d_{11}$ for quartz) showing the advantage of our ferroelectric metamaterial compared to a range of natural and synthetic piezoelectric materials.
ical stimuli at the tip of the structure produced ~0.75 V output, while the same stimuli at the side yielded negligible electricity. For a bone printed along the short axis, stimuli at the tip yielded negligible output but induced ~0.6 V voltage when applied toward the side of the bone. Such an anisotropic piezoelectricity offers a possibility of mimicking real bone geometrically and functionally, which is essential for tissue engineering.

The modulus of the printed structures could be readily tuned to match the values of natural bones. As the electrode layer increased from 0 to 100% of the entire structure, the compressive modulus was tuned from 0.47 to 1.48 GPa (Figure S17a,b), where equal thicknesses of ferroelectric and electrode layers (the ratio used in our artificial bones) yielded a compressive modulus of ~0.78 GPa (Figure 4c-i). In natural bones, the trabecular bone (cancellous bone) has a much lower modulus (0.12–1.1 GPa) than the cortical bone due to its significantly higher porosity. Inverse-designed metamaterials can match both the topology and mechanical properties of bone by tuning the porosity. Analogously, introducing porosity would further lower the compressive modulus of a printed bone-like structure (Figure 4c-ii and Figure S17c). Therefore, by tuning both composition and porosity, the modulus (0.18–1.48 GPa) (Figure 4d) of structure achieved by the 3D printing technique could well-match the counterparts of trabecular bone. A higher modulus, to the level of cortical bone (10–20 GPa), could be still obtained by selecting more rigid polymer matrixes (such as liquid crystal polymer with modulus over 10 GPA) as the printing composite matrix. Theoretically, the porosity does not influence the overall $d_{31}$ value but can raise the voltage output as a result of the lowered modulus. Practically, this relation held well at relatively low porosity (<50%) but deviated at a higher positivity (75%), possibly due to more electric breakdowns or less electric field screening as the pore volume expanded (Section S2 and Figure S18).

Owing to its superior piezoelectric response and tunable mechanical property, our 3D-printed lamellar ferroelectric metamaterial will excel at artificial bone implants and beyond compared to other natural and synthetic piezoelectric materials. As shown in Figure 4e, most natural piezoelectric materials, such as bones and cellulose, have a rather weak piezoelectric property, though their mechanical property is desirable. Glycine, a typical piezoelectric biomaterial, possesses appreciable piezoelectricity but a high fragility. The highest piezoelectric property is typically offered by piezoceramics. Nevertheless, the high brittleness associated with their ceramic nature yields undesired toughness and hardness. This comparison shows that our ferroelectric metamaterial stands at a position, where both high piezoelectric performance and excellent durability can be expected.

**CONCLUSION**

In summary, through a low-voltage-assisted 3D printing platform, a lamellar ferroelectric metamaterial was created with exceptional piezoelectricity and fracture toughness. Ferroelectric PVDF-HFP/Li-KNN and conductive PLA/CB composites were developed, mimicking the soft biodehensive and tough aragonites in nacre, respectively, as the building blocks to construct a lamellar heterostructure. The design of alternating ferroelectric and electrode layers during printing allowed the application of a reasonably low in situ poling voltage to effectively and selectively pole each ferroelectric layer independent of the size and number of layers. The interdigitated configuration and uniform quality among layers enabled the effective accumulation of piezoelectric charges from each layer. Thus, a significantly enhanced $d_{31}$ of over 150 pC N$^{-1}$ was achieved from a 25-ferro-layer structure, reaching the same level of piezoceramics. The nacre-mimetic structure together with the strong interfacial adhesion brought high resistance to crack propagation and achieved a super high fracture toughness of 5.5 MPa m$^{1/2}$, exceeding most natural and synthetic piezoelectric materials. It should be noted that common imperfections by FDM 3d printing, such as blobs and pores, do exist in our prints. A higher piezoelectric and mechanical performance may be expected if these defects could be minimized, for example by leveraging the advanced strategies developed in general FDM procedures to achieve optimized printing dynamics. On the basis of this structure, full-sized piezoelectric bone-like structures were created with anisotropic piezoelectricity, strong toughness, and tunable modulus. The further integration of multinozzle setup and complex 3D lattice design may enable multidimensional piezoelectricity independent of the printing sequence and direction, showing the ultimate value of additive manufacturing. This versatile fabrication technique and materials design strategy will make a big leap toward practical applications of 3D-printed functional piezoelectric materials and devices. Beyond the biological implants, the applications potential of the printed metamaterials may include energy harvesters, power sources for small electronics, self-powered sensors, and therapeutic electro-stimulators.

**EXPERIMENTAL PROCEDURES**

**Particles Preparation, Surface Modification, and Characterization.** Lithium-doped potassium sodium niobate (Li-KNN, $K_{0.95}Li_{0.05}NbO_3$) was synthesized by a conventional solid-state reaction method. Raw materials including potassium carbonate ($K_2CO_3$, > 99%, Sigma), sodium carbonate ($Na_2CO_3$, > 99.5%, Sigma), lithium carbonate ($Li_2CO_3$, 99.999%, Strem Chemicals, Inc.), and niobium oxide ($Nb_2O_5$, > 99.9%, Alfa Aesar) were uniformly mixed in in a molar ratio of 47:47:6:100. They were milled in 250 mL nylon jar with ZrO$_2$ balls for 6 h through a laboratory planetary ball mill system (BM4X-V20L, Col-Int Tech, LLC), using ethanol as a medium. The mixture was then dried at 210 °C for 2 h to remove absorbed moisture. The dried mixture was then calcined at 1100 °C in a Muffle furnace in ambient environment for 4 h followed by slowly cooling to room temperature to form high-purity ceramics. Li-KNN ceramics were grinded to microparticles (MPs) by a SPEX 8765 Cryogenic Grinder. The MPs were first refluxed with H$_2$O$_2$ solution (30%) at 105 °C for 2 h to add hydroxyl group onto the surface. The collected samples through centrifuge (3300 r/min for 15 min, with a relative centrifugal force (RCF) of 1380 G) were rinsed with DI water three times and dried in oven (80 °C for overnight). The Li-KNN MPs were characterized by X-ray diffraction (XRD) patterns, which were acquired from a Bruker D8 Discovery with Cu Kα radiation. A Zeiss LEO 1530 field-emission electron microscope was utilized for the observations of MPs morphology and element analysis through energy-dispersive X-ray spectroscopy (EDS) mapping.

**Composite Preparation and Filament Extrusion.** Surface-modified MPs were mixed with PVDF-HFP pellets (Solef 21508, PolyK Technologies, LLC). Mixtures were added into $N,N$-dimethylformamide (DMF, > 99.8%, Sigma)
solvent at 80 °C for 3 h with stirring to form a uniform solution (15 wt % concentration), which would be casted into glass dish to form composite film after evaporating solvent at 70 °C overnight. The films were grinded into fine powders by a SPEX 6875 Cryogenic Grinder. The conductive composite was a mixture of carbon black (Ketjen Black, EC600JD, ~6 wt %) with poly(lactic acid) (Natureworks 4043D PLA). The mixture was added into chloroform (∼99.8%, Sigma) solvent at 45 °C for 3 h with stirring to form a uniform solution (5 wt % concentration), which was casted into a glass dish to form a composite film after evaporating solvent at 60 °C overnight, and then, the films were grinded into fine powders by a SPEX 6875 Cryogenic Grinder. With grinded fine powders as raw materials, the filament with constant diameter around 2.6–2.8 mm was extruded through a customized single-screw polymer extruder (built based on Filastruder kit with 3.00 mm nozzle and 400 μm filter) with the temperature of header set at 170–230 °C and collect by a customized winder (built based on Filawinder kit) with spool. A laser sensor was utilized for filament diameter control. The extruder system and extruded filament are displayed in Figure S6.

3D Printing. Ferroelectric composite and conductive composite (a mixture of carbon black with poly(lactic acid) (Natureworks 4043D PLA)) were printed by a customized fused deposition modeling (FDM) 3D printer (the step accuracy in the Z direction and layer resolution of the 3D printer (for ideal materials) are 2.5 and 20 μm, respectively). An inner electric field was built by connecting the print core and printing bed covered with copper foil to a high voltage source (30 kV, 10W). A thin layer of PVA (Elmer’s Disappearing Purple Glue Stick) was applied on the copper foil to enhance the adhesion of the first printing layer. The ferroelectric composite was printed at a speed of 10 mm/s (110% materials flow) at a nozzle (0.4–0.8 mm diameter) temperature of 260 °C. The conductive composite was printed at a speed of 20 mm/s (100% materials flow) with a nozzle (0.4–0.8 mm diameter) temperature of 220 °C. The nozzle to substrate distance was adjusted through the automatic leveling of build plate by the 3D printer.

Piezoelectricity Measurement. The direct piezoelectric $d_{33}$ coefficients of 3D-printed ferroelectric structures were measured using a quasistatic $d_{33}$ piezometer (PKD3-2000-F10N, PolyK Technologies, LLC) under a static force around 3 N and a dynamic force of 0.25 N. The polarization–electric field ($P$–$E$) curve of the 3D-printed ferroelectric film was evaluated on a ferroelectric analyzer (CPE1801-10 kV, PolyK Technologies, LLC, Philipsburg, PA) under a frequency of 1 Hz and a maximum electric field of 25 MV/m.

Electric Output Measurements. The open-circuit voltage outputs ($V_{OC}$) of 3D-printed structures were measured by connecting probes of a multimeter (DMM 6500, Keithley) to electrodes. The short-circuit current ($I_{SC}$) was measured by a low-noise current preamplifier (Stanford Research Systems, model SR570) connected with LabVIEW system in a computer. The charge outputs (Q) of 3D-printed structures were measured by a high-precision 51/2-digit electrometer (Keithley 6514).

Mechanical Stimuli Application and Force Quantification. An instant force of 100 N (peak value) was applied to the 3D-printed ferroelectric structures by an actuator (LinMot USA, Inc.) at 1 Hz controlled by a computer. The tip of the actuator contacting the ferroelectric print has a surface area of ∼1.8 cm$^2$. The force was quantified by a portable sensor measurement system (compression piezoelectric sensor (CL-YD-303) integrated with a four-channel dynamic signal acquisition module (NI 9234) and compact data acquisition chassis (NI, cDAQ-9171)).

Modulus Measurement. The tensile modulus of 3D-printed dog-bone structures (8 cm × 1 cm × 0.8 mm) were measured by a tensile test (ASTM D638) in MTS Criterion Model 43. The compressive modulus of 3D-printed cylinders (1 cm × 1 cm × 2.5 cm) was measured by a compression test (ASTM D695) in MTS Criterion Model 43. The flexural moduli of 3D-printed rectangular beam and commercial PVDF beam were measured by a three-point bending test (ASTM D790) in MTS Criterion Model 43.

Interface Bonding Characterization. The interface adhesion could be measured through a Trousier Peel Test (ASTM F88), which applies to flexible specimens, in MTS Criterion Model 43. Bilayers with a size of 1 cm × 8 cm × 0.4 mm were printed with each layer having a thickness of 200 μm. An initial cleft around 2 cm length was introduced between the two adhesive layers. The free ends of the two layers were mounted on the grippers and pulled in opposite directions at a constant rate (10 mm/min), while the force to peel them off was continuously recorded as the cleft progresses toward the other end (see Figure S14). The exposed surfaces of specimen after the peeling test were characterized by SEM and EDS. The detailed calculation of interfacial adhesion energy is revealed in the Supporting Information.

Toughness Characterization. The fracture toughness of 3D-printed samples was performed through single-edge notchched bend (SENB) tests (ASTM D5045) in an MTS Criterion Model 43 system. The 3D-printed samples have a length of 4 cm, a width of 5 mm, and a thickness of 5 mm. A notch depth of 3 mm was created in the sample. The SENB test has the same setup as the three-point bending test, and the velocity of compression was 1 mm min$^{-1}$ with a span support of 2.5 cm. The detailed calculation of fracture toughness $K_J$ for stable crack propagation is exhibited in the Supporting Information.

Finite Element Analysis. The voltage potential and inner electric field during 3D printing were simulated by the commercial finite element analysis (FEA) software ANSYS 19.2 Version.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.nano.1c05003.

Discussions of crystallinity calculation of printed PVDF-HFP and PVDF, structural influence on metamaterials piezoelectricity, in-series model printing, adhesion energy calculation, fracture toughness calculation, and mechanism behind toughness enhancement, figures of PVDF and PVDF-HFP printing and properties comparison, characterization of Li-KNN materials, electrical conductivity measurement of the electrode layer, ferroelectric mematerial interface investigation, fabrication and properties of PVDF-HFP/Li-KNN printing raw material, piezoelectric property of a single ferroelectric layer, in situ poling electric potential design, two different printing processes of the multilayered structure, mechanical moduli of PLA/CB and PVDF-HFP/Li-KNN films, mechanical stimuli and short circuit current,
open circuit voltage measured from metamaterials, piezoelectricity of 25-ferro-layered metamaterial, direct printing in situ poled ferroelectric material with in-series connection of all ferroelectric layers, interfacial adhesion characterization of printed bilayer structures, PLA/CB peeling surface observation, toughness enhancement and mechanism, mechanical modulus tuning, influence of porosity on piezoelectricity, and table of estimated equivalent dielectric constants $\varepsilon_r$ and piezoelectric voltage constants $g_{33}$ of printed structures (PDF)

Video of extrusion of ferroelectric composite by a customized extruder system (MOV)

Video of current output of three-unit ferroelectric structure under 100 N mechanical stimuli (MOV)

Video of video of light 10 LED bulbs by 3D-printed bulk ferroelectric structure (MOV)

Video of low-voltage-assisted printing of 25-unit scaled ferroelectric structure (MOV)

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Author Contributions
J.L. and X.W. conceived the idea, initiated this study, and designed the research program. J.L., F.Y., and Y.L. performed the ferroelectric structure printing, electromechanical measurement, and data analysis. Y.D. carried out EIS measurement. J.L. and Y.W. carried out SEM, EDS, and XRD characterizations. J.L. did the PE-loop and $d_{33}$ measurement. F.Y. performed the simulation. J.L. and X.W. wrote the manuscript. All authors reviewed and commented on the manuscript.

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REFERENCES


